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High oxidation state aqueous organometallics. Formation and structure of an oxo-centred $\text{Cp}^*\text{Mo}^{\text{V}}$ trinuclear cation by chemical reduction of $\text{Cp}^*_2\text{Mo}_2\text{O}_5$.

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By zinc/ CF_3COOH reduction in $\text{MeOH-H}_2\text{O}$, compound $\text{Cp}^*_2\text{Mo}_2\text{O}_5$ yields a salt which is composed of $[\text{Cp}^*_3\text{Mo}_3\text{O}_4(\text{O}_2\text{CCF}_3)_3]^+$ and $[\text{Zn}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$ ions after crystallisation from $\text{THF/Et}_2\text{O}$.

High oxidation state organometallic chemistry is now a mature field with important applications to a variety of catalytic transformations.^{1, 2} Although many compounds in this class are stable in an aqueous environment and some have even been synthesised in water, their aqueous chemistry has rarely been investigated. Complex $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]^{3, 4}$ is one such example. We have recently described an improved aqueous synthesis,⁵ the speciation of this compound in water⁶ which highlighted the new species $[\text{Cp}^*\text{MoO}_2(\text{OH})]$ and $[\text{Cp}^*\text{MoO}_2]^+$, and an exploratory aqueous reductive electrochemistry study. An on-line voltammetric-ESMS investigation has indicated the formation of a wealth of new mixed oxo- Cp^* complexes in oxidation states down to IV.⁷ Therefore, we are now proceeding to explore synthetic chemical reductions under a variety of conditions. The first product that we have isolated, showing unexpected and unusual features, is reported in this contribution.

The compound is generated by zinc reduction in $\text{MeOH-H}_2\text{O}$ containing trifluoroacetic acid and air-stable single crystals have been obtained from $\text{THF-Et}_2\text{O}$.[†] The structure of the compound has been elucidated by X-ray crystallography.[‡] It is composed of $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-O}_2\text{CCF}_3)_3]^+$ (Fig. 1) and $[\text{Zn}_2(\mu_2\text{-O}_2\text{CCF}_3)_4(\text{O}_2\text{CCF}_3)_2]^{2-}$ (Fig. 2) ions. The cation, of ideal C_{3v} symmetry, sits on a general position, while the dianion lies on inversion centers. The cation features an oxo-capped equilateral Mo_3 triangle where each metal has the formal oxidation V (3 cluster electrons). Each edge is further bridged by an oxo and a trifluoroacetate ligand, and an $\eta^3\text{-Cp}^*$ ligand completes each metal's coordination sphere. No previous example seems available of a Mo_3 cluster, whatever the coordination sphere and geometry, where the metal oxidation state is as high as V.

The central Mo_3O_4 core is a quite typical archetype for Mo_3 clusters, but is mostly found for clusters containing 6 metal electrons (Mo^{IV}), e.g. the $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ aqua ion.⁸ Examples have also been described for lower oxidation states, notably 8-electrons ($\text{Mo}_3^{\text{III,III,IV}}$), but not for higher ones.⁹ Previously reported clusters featuring triangular $(\text{Cp}^*\text{Mo})_3$ units include $[(\text{Cp}^*\text{Mo})_3(\mu_2\text{-OH})_n(\mu_2\text{-O})_{6-n}]^{2+}$ ($n = 4, 5, 6$; e.g. 5, 6 and 7-electron clusters),¹⁰ the two related $[\text{Cp}^*_4\text{Mo}_5\text{O}_{11}]$ and $[\text{Cp}^*_6\text{Mo}_8\text{O}_{16}]$ clusters^{10, 11} containing the same 4-electron $\text{Mo}_3(\mu_2\text{-O})_6$ core, and $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-O})(\mu_2\text{-Cl})_4\text{Cl}_3]$.¹² None of these compounds contains a Mo_3O_4 core, nor has any of them the oxidation state V for all Mo centres. The related Mo^{IV} clusters $[\text{Cp}_3\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_4]^{+13}$ and $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-CH})(\mu_2\text{-CH}_2)(\mu_2\text{-O})_2]^{14}$ are also known. The $\text{Mo}_3(\mu_2\text{-O}_2\text{CR})_3$ unit has precedents in non organometallic complexes with 6-9 cluster electrons, none

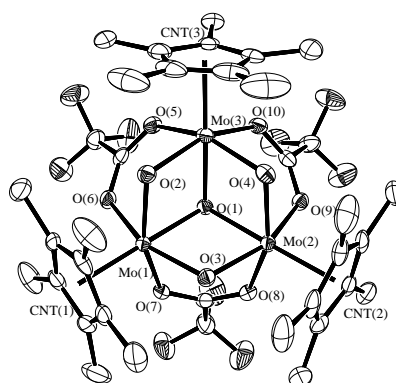


Fig. 1 ORTEP view of the $[\text{Cp}^*_3\text{Mo}_3\text{O}_4(\text{O}_2\text{CCF}_3)_3]^+$ cation. Relevant averaged parameters: Mo-Mo, 3.1287(15); Mo-CNT (Cp* centroid), 2.069(5); Mo-O(1), 2.032(6); Mo-(μ_2 -O), 1.95(1); Mo-O(acetate), 2.183(10); C-O, 1.249(4) Å; CNT-Mo-O(1), 177.63(12); Mo-(μ_2 -O)-Mo', 106.9(4); Mo-(μ_3 -O)-Mo', 100.7(3)°.

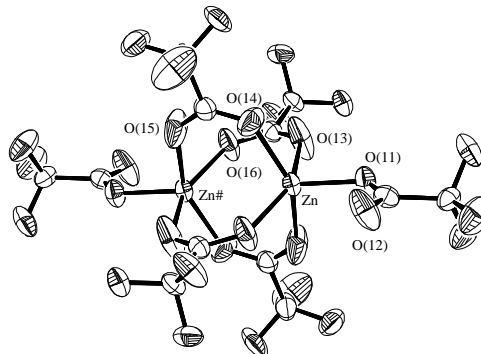
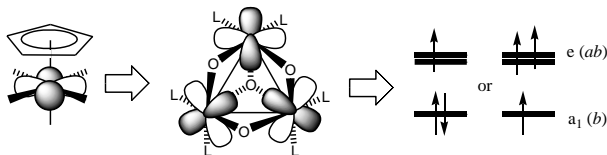


Fig. 2 ORTEP view of the $[\text{Zn}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$ anion. Relevant averaged parameters: Zn...Zn, 3.228(5); Zn-O(bridging), 2.05(2); Zn-O(terminal), 1.926(3); C-O(br.), 1.214(14); C-O(term.), 1.243(5); C=O, 1.207(5) Å; O(br.)-Zn-O(br.)' (*cis*), 86.4(9); O(br.)-Zn-O(br.)' (*trans*), 150.9(2), O(11)-Zn-Zn#, 166.7(1)°.

of which contains a $\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-O})_4$ core.¹⁵⁻¹⁸ The closest relative appears to be $[\text{Mo}_3\text{O}_4(\text{O}_2\text{CH})_8]^{4-}$ (another compound of Mo^{IV}), having a single bridging and seven terminal (η^1) formate ligands.¹⁹

The Mo-Mo distance indicates little or no direct metal-metal bonding. The absence of a strong interaction may be easily understood on a qualitative basis, imagining the formal assembly of the $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-O})(\mu_2\text{-O})_3\text{L}_6]$ cluster (L = terminal ligand) from three mononuclear CpML₅ fragments (see Scheme 1). The Cp* ligand occupies the position *trans* to the capping O atom for each metal. Only one orbital (d_{xy}) is available to accommodate metal electrons and the three resulting cluster

orbitals can only establish weak π/δ type interactions (see Scheme 1). The most favourable scenario for metal-metal bonding features two weakly bonding (a_1) and one antibonding (e) electron. Both $[\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-O})_3\text{L}_9]$ (Mo-Mo around 2.5 Å for 6 cluster electrons) and $[(\text{Cp}^*\text{Mo})_3(\mu\text{-O})_6]$ type clusters (Mo-Mo = 2.7–2.8 Å for 4 to 6 electrons), on the other hand, possess more and better oriented orbitals for metal-metal bonding.^{10,20} The Mo-($\mu_2\text{-O}$), Mo-($\mu_3\text{-O}$) and Mo-O(COCF₃) distances are slightly longer in our $[(\text{Cp}^*\text{Mo})_3\text{Mo}_3\text{O}_4(\text{O}_2\text{CCF}_3)_3]^+$ cluster relative to the previously cited related Mo^{IV} clusters. The weaker Mo-Mo interactions probably play a more important role than the expected smaller ionic radius for determining these distances.



Scheme 1. Orbital interactions in $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-O})(\mu_2\text{-O})_3\text{L}_6]$ clusters

The $[\text{Zn}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$ structure is also worthy of brief comment. Structurally characterised lantern-type $\text{Zn}_2(\mu\text{-O}_2\text{CR})_4\text{L}_2$ precedents ($\text{R} = \text{CH}_3$, $\text{CH}=\text{CHCH}_3$; $\text{L} = \text{py}$, py-4-CN , quin) show slightly shorter Zn-Zn distances (2.89–2.98 Å),^{21–23} though a direct bonding interaction is precluded by the closed-shell configuration of Zn^{2+} . An incipient interaction between the Zn^{2+} centres and the "free" C=O groups may be responsible for a slight misalignment between the Zn-O(term.) and Zn-Zn axes.

Given the low coordinating ability of CF_3COO^- , its facile dissociation in an aqueous environment, leaving a $[(\text{Cp}^*\text{Mo})_3\text{O}_4]^{4+}$ core, may be expected. However, an electrospray mass spectrometric (ESMS) study of the compound (positive mode) shows the envelope of the structurally characterised cation in either THF, MeCN, or MeCN-MeOH (see Fig. 3a).⁸ MSⁿ investigations reveal the successive loss of $\text{Cp}^*\text{MoO}_2(\text{O}_2\text{CCF}_3)$, CF_3COOH , CF_3COOH , and H_2O . Under negative detection mode, the major envelope corresponds to a $[(\text{Cp}^*\text{Mo})_3(\text{O})_4(\text{O}_2\text{CCF}_3)_5]^-$ species which derives from the transfer of two CF_3COO^- ions from the Zn dianion. When the same experiment was carried out in the presence of 0.28 M CF_3COOH , however, the monoanions $[\text{Zn}(\text{O}_2\text{CCF}_3)_3]^-$ and $[\text{Zn}_2(\text{O}_2\text{CCF}_3)_5]^-$ were observed (see Fig. 3b).

The $\text{Cp}^*\text{Mo}^{\text{V}}$ moiety in combination with oxo ligands is

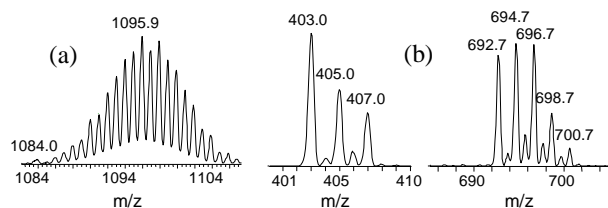


Fig. 3. Excerpts of the ESMS of the title compound in MeCN in the presence of 0.28 M CF_3COOH . (a) Positive detection mode. (b) Negative detection mode.

already known in dinuclear (e.g. $[\text{Cp}^*\text{MoO}_2]_2$)²⁴ and mononuclear (e.g. $[\text{Cp}^*\text{MoOCl}_2]$)²⁵ complexes. Dinuclear and mononuclear oxo-carboxylato $\text{Cp}^*\text{Mo}^{\text{V}}$ species were also detected in our recent EC-ESMS study,⁷ whereas a trinuclear one was not. Whether a relationship between these smaller fragments and the trinuclear complex shown here exists and under which conditions one may be able to interconvert these species are questions for future investigations. Another interesting and related question is the lability of the capping oxo ligand, since this is extremely inert in the large class of Mo^{IV}₃O₄ clusters.⁸ We also wish to isolate larger quantities of salts containing this cation to investigate its magnetic properties.

As a final remark, we underline the robustness of the

Cp^*Mo bond, which remains intact upon long reaction times under strongly acidic aqueous conditions. This feature is encouraging for the future development of catalytic and electrocatalytic processes with Cp^*Mo systems in an aqueous environment. JG and RP thank Arc-en-Ciel/Keshet and FD thanks TUBITAK-NATO for travel grants.

Notes and references

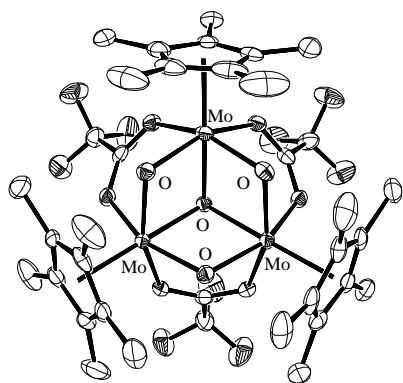
[†] $[(\text{Cp}^*\text{Mo})_2\text{O}_5]$ (0.15 g, 0.28 mmol) dissolved in MeOH:H₂O (1:1, 10 ml) was treated under argon with Zn powder (1.5 g, 23 mmol) and concentrated CF_3COOH (10 drops). Three-day stirring at rt yielded a green suspension. After filtration and drying, the solid was extracted with THF and, after filtration, addition of heptane yielded a blue precipitate. A small amount of single crystals of the title compound were obtained by diffusion of an ether layer to a blue THF solution at rt.

[‡] Crystal data. $\text{C}_{42}\text{H}_{45}\text{F}_{18}\text{O}_{16}\text{Mo}_3\text{Zn}$, $M = 1500.97$, monoclinic, $a = 11.8671(1)$, $b = 11.7975(1)$, $c = 37.6903(5)$ Å, $\beta = 95.767(1)^\circ$, $U = 5250.01(9)$ Å³, $T = 110$ K, space group $P2_1/n$ (no.14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.28$ mm⁻¹, 20526 reflections measured, 11521 unique ($R_{\text{int}} = 0.039$) which were used in all calculations. The final $wR(F^2)$ was 0.096 (all data).

[§] MS investigations were carried out with a Finnigan (San Jose, USA) LCQ quadrupole ion trap mass spectrometer equipped with a Protana (Odense, Denmark) nano-electrospray ionization (ESI) interface. Tip and sampling cone potentials were -1.5 kV and -50 V (negative mode), 1.5 kV and 23 V (positive mode), respectively. The mass analyzer was scanned from m/z 100 to 2000 (5 total microscans). Maximum injection time into ion trap was 50 ms. Sample injection flow rate was 1 $\mu\text{L}\cdot\text{min}^{-1}$.

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Abstract for the Table of Contents



By zinc/ CF_3COOH reduction in $\text{MeOH-H}_2\text{O}$, compound $\text{Cp}^*_2\text{Mo}_2\text{O}_5$ yields an oxo-centred, C_{3v} -symmetric, trinuclear cation of Mo^{V} , whose coordination environment and electronic structure preclude the establishment of strong metal-metal interactions.